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RELATIONSHIPS BETWEEN SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, AND EXPANSION IN THE DETERMINATION OF THE ALKALI REACTIVITY OF BASALTIC ROCKS

S.A. Marfil,[1,2]* P.J. Maiza,[3]* A.L. Bengochea,[3]* J.D. Sota,[4]† and O.R. Batic[2]†
*Universidad Nacional del Sur, San Juan 670, (8000) Bahía Blanca, Argentina
†LEMIT, Calle 52, entre 121 y 122, (1900) La Plata, Argentina

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ABSTRACT

The purpose of this work is to attempt to establish the relationship between the chemical elements leached out of basaltic rocks and the expansion measured on mortar bars by the ASTM C9 P214 method.

Seventeen basalt samples from different locations in Argentina were selected. Solubilized SiO_2 was determined by the chemical test method (ASTM C-289). An aliquot of the solution was analyzed by ICP, indicating the presence of Al_2O_3, Fe_2O_3, CaO, K_2O, MgO, TiO_2, and MnO.

The results obtained were statistically treated by the Principal Components method in order to determine whether there is a relationship between each of the analyzed elements and the expansion and, if any, their degree of participation.

It was concluded that expansion is closely related to the dissolved silica contributed by the deleterious mineralogical components of basaltic rocks, especially volcanic glass and its alteration products, and poorly crystallized silica. The iron and calcium content does not have any influence on the reactivity. High values of solubilized silica would indicate that the basaltic rock has undergone an intense devitrification and/or silicification. *© 1998 Elsevier Science Ltd*

Introduction

Earlier studies carried out on basaltic aggregates clearly showed the deleterious reactive nature of some of them with respect to the alkalis. Several test methods, such as the accelerated method proposed by the NBRI and the chemical and petrographical methods, were used. The first results were rather varied, as aggregates ranged from totally innocuous to highly reactive. Eventually, it could be determined that volcanic glass, montmorillonite-

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[1]To whom correspondence should be addressed.
[2]Researcher CIC
[3]Researcher CONICET
[4]Senior Professional CIC

TABLE 1
Results from chemical analyses and expansion according to ASTM C9 P214.

Sample	No.	SiO_2 (mg)	K_2O (mg)	Al_2O_3 (mg)	Fe_2O_3 (mg)	CaO (mg)	Expansion (%)
La Garrapata	1	3.03	2.60	1.65	0.018	0.015	0.073*
Los Cóndores	2	3.95	3.79	1.90	0.015	0.014	0.063*
Compact Comallo	3	7.27	9.78	1.80	0.029	0.015	0.070*
Aguada de Guerra	4	13.33	0.52	3.10	0.008	0.018	0.111*
Praguaniyeu nodules	5	18.00	1.04	0.74	0.006	<0.001	0.044
Porous Comallo	6	18.17	6.79	2.31	0.008	0.014	0.070*
Yacyretá	7	19.77	1.21	0.51	0.013	0.007	0.343*
La Pasarela	8	20.78	4.16	0.86	0.012	0.002	0.111*
Cerro Mesa	9	32.09	3.30	1.89	0.007	0.014	0.439
Porous Teniente Maza	10	34.90	1.29	1.02	0.009	<0.001	0.407
Compact Teniente Maza	11	38.10	1.22	1.18	0.018	<0.001	0.407
El Cuy	12	38.40	0.36	1.63	0.040	<0.001	1.075
Praguaniyeu plateau	13	43.40	2.38	1.50	0.020	<0.001	0.965
La Calera	14	45.09	0.32	1.03	0.015	0.018	0.538*
Lower Pajalta	15	46.80	1.72	1.26	0.027	<0.001	0.470
Middle Pajalta	16	67.40	0.25	0.61	0.004	0.013	0.603
Upper Pajalta	17	78.40	1.29	0.38	0.018	0.016	0.651

*see Ref. 1

type clays, and poorly crystallized silica are mainly responsible for the aggregate reactivity (1,2). Similar results have been reported around the world in the literature (3,4).

This work attempts to establish the relationship between the chemical elements leached out of basaltic rocks when they are treated as prescribed by ASTM C-289 and the expansion measured on mortar bars by the accelerated method proposed by ASTM C9 P214 (5), which is similar to the NBRI method and has been standardized as ASTM C1260–94 (6). To that end, the analytical results obtained were treated by the statistical method of Principal Components.

Materials and Methods

Seventeen basalt samples from different locations in Argentina were used. Those termed compact Comallo, porous Comallo, Aguada de Guerra, Praguaniyeu with nodules, Praguaniyeu plateau, Cerro Mesa, compact Teniente Maza, porous Teniente Maza, El Cuy, La Calera, lower Pajalta, middle Pajalta, and upper Pajalta are from Río Negro province. La Garrapata is from San Luis province, Los Cóndores is from Córdoba province, Yacyretá is from Misiones province, and La Pasarela is from Mendoza province. The exact geographic location of the deposit and the petrographic-mineralogical study were published in former papers (1,2), as well as the expansion of eight of them (1).

The ASTM C-289 test method (7) was used in the chemical analysis to determine which elements were involved in the deleterious reaction. All studied samples were treated as follows: a 25-g sample crushed to a size between 0.300-mm (No. 50) and 0.150-mm (No. 100) IRAM sieves was taken. As prescribed in the method, 25 mL of 1N

TABLE 2
Correlation matrix.

1.000	−.492	−.546	.035	−.097	.721
−.492	1.000	.343	.126	.228	−.462
−.546	.343	1.000	.057	.348	−.304
.035	.126	.057	1.000	−.267	.454
−.097	.228	.348	−.267	1.000	−.329
.721	−.462	−.304	.454	−.329	1.000

Na(OH) solution were added and the sample was left to digest in a gravity convection oven at 80°C for 24 h. It was then filtered, a 10-mL aliquot was taken and made up to 200 mL. Solubilized silica was determined and the content of Al_2O_3, Fe_2O_3, CaO, K_2O, MgO, TiO_2, and MnO was analyzed by inductively coupled plasma emission spectrometry (ICP). The latter three oxides were not included in the statistical treatment, as the quantities detected were below a hundredth of a milligram. At the same time, the mortar bar accelerated test was applied to the aggregate in accordance with the ASTM C-9 P-214 method. Results are given in Table 1.

Data were treated by the Principal Components statistical method, which consists of simplifying the structure of variables in a matrix, which can be either a covariance or a correlation matrix. The correlation matrix was used in this work to impart the same weight to all variables, as data had been obtained in two different units (mg and %).

The Principal Components method defines new variables from the matrix, which result in a linear combination of the original ones, in such a way that each of them concentrates the highest variability and they are linearly independent.

Statistical Study

A statistical study was conducted with the data from Table 1, applying the Principal Components method, with the following correlation matrix being obtained (Table 2).

The variance percentage associated with each Principal Component is shown in Table 3.

The reconstruction percentage of each variable using the first four components is very high: SiO_2 = 91.52%; K_2O = 92.53%; Al_2O_3 = 93.40%; Fe_2O_3 = 90.81%; CaO = 94.66%; and expansion = 91.71%. Therefore, the first four components were selected, which represents 92.44% of the total variance.

Table 4 is good in illustrating that the first component is given by SiO_2 + expansion vs. K_2O, Al_2O_3, which represents 44% of the total variance of the model, showing that the silica present in the solution is directly related to expansion.

The second component is given almost exclusively by Fe_2O_3 and represents 22% of the

TABLE 3
Associated variance.

Component No.	I	II	III	IV	V	VI
Associated variance %	44.068	21.965	15.361	11.044	5.581	1.981

TABLE 4
Correlation between variables and the first four components.

Variable		PCI	PCII	PCIII	PCIV
SiO_2	X1	0.83372	−0.24288	0.33487	−0.22136
K_2O	X2	−0.67761	0.37591	−0.02548	−0.56939
Al_2O_3	X3	−0.67197	0.30148	0.38787	0.49100
Fe_2O_3	X4	0.25809	0.89737	0.16926	−0.08706
CaO	X5	−0.49751	−0.37547	0.72226	−0.19081
Expansion	X6	0.85098	0.28367	0.32883	0.06605

total variance. The graph of variables on the plane of the first two components shown in Figure 1 serves as an illustration of the above statements.

CaO is represented in the third principal component, which implies 15% of the total variance. The variables on the plane of the first and third component are depicted in Figure 2.

The first three components account for 81% of the total variance, although the K_2O (60%) and Al_2O_3 (69.29%) variables are not well represented. In fact, the fourth component represents the inverse ratio between these two variables. Although the fourth component itself represents 11% of the total variance, if it is considered together with the former three, 90% of the total variance can be exceeded, as shown in Figure 3.

Centered coordinates of the samples, represented by the first four principal components, are shown in Table 5. These results are plotted in the graphs in Figures 4, 5, and 6.

The samples on the plane of the first two components are represented in Figure 4, showing that those which have positive values in Y1 expanded more and have a higher SiO_2 content, hence they will behave as potentially reactive.

Samples with negative values in Y1 have a higher K_2O and Al_2O_3 content and less expansion and solubilized silica. They will behave as inert. Y2 represents Fe_2O_3 content, which is independent of expansion and silica content.

Figures 5 and 6 show the graph of samples on the plane of the first-third and first-fourth components, respectively. Samples with higher Y3 have a high CaO content. Positive values

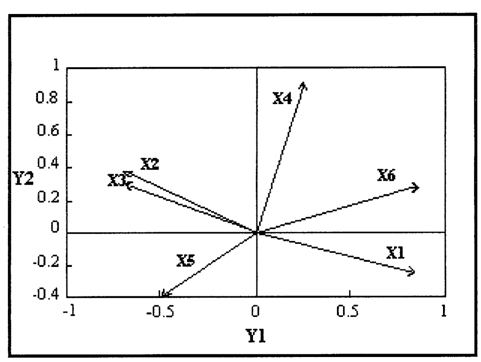

FIG. 1.
Variable correlation in Y1–Y2.

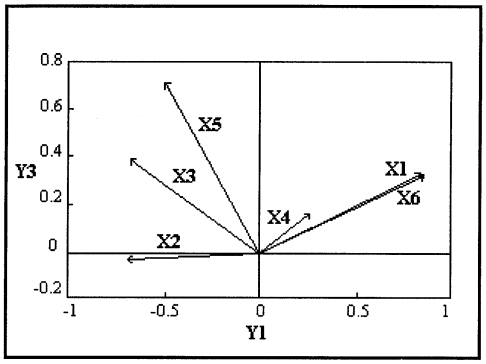

FIG. 2.
Variable correlation in Y1–Y3.

of Y4 are related to samples with a high alumina content, whereas negative values indicate high K_2O content.

Conclusions

From the study of the relationship between aggregate reactivity, shown by expansion, and leached elements, when subjected to a similar treatment to that prescribed by ASTM C-289 recommendation, it can be concluded that:

1. There is a correlation between expansion, measured in accordance with ASTM C9 P214 method, at 28 days, and solubilized silica from basaltic rocks.
2. Samples from Yacyretá (No. 7), Teniente Maza (No. 10, 11), El Cuy (No. 12), Praguaniyeu plateau (No. 13), La Calera (No. 14), and Pajalta (No. 15, 16, and 17), showed higher expansion and solubilized silica content. On the other hand, samples from Comallo (No. 6), Aguada de Guerra (No. 4), Los Cóndores (No. 2), Garrapata (No. 1), La Pasarela (No. 8), Praguaniyeu with nodules (No. 5), and Cerro Mesa (No. 9) showed less expansion and a prevalence of K_2O, alumina, and CaO over silica.

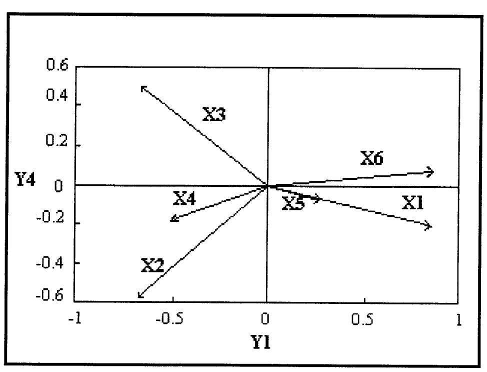

FIG. 3.
Variable correlation in Y1–Y4.

TABLE 5
Centered coordinates of samples for the first four principal components.

Sample No.	PCI	PCII	PCIII	PCIV
1	−1.552	0.112	0.035	0.263
2	−1.924	0.108	0.082	0.179
3	−2.536	1.924	0.298	−1.752
4	−2.152	−0.685	1.147	1.944
5	−0.057	−0.941	−1.935	0.307
6	−2.406	−0.092	0.331	−0.374
7	0.404	−0.552	−0.907	−0.174
8	−0.433	−0.092	−1.533	−0.574
9	−0.686	−0.661	0.745	0.149
10	0.781	−0.472	−1.064	0.322
11	0.920	0.254	−0.760	0.340
12	2.257	2.660	0.631	0.870
13	1.614	1.108	0.134	0.336
14	0.727	−0.941	1.214	−0.142
15	1.260	1.098	−0.334	0.067
16	1.671	−1.946	0.638	−0.448
17	2.112	−0.882	1.278	−1.311

3. Fe_2O_3 is ubiquitous and bears no relationship with expansion or silica.
4. The identification of migrating cations due to Na(OH) attack enables the determination of which of the mineralogical components leached out of basaltic rocks are. For instance, a high SiO_2 content with lower quantities of Al_2O_3, K_2O, and CaO would indicate that the alterated phase would be volcanic glass and that such rock may have also undergone an intense devitrification and/or silicification.
5. Although these conclusions apply to the 17 basalt samples analyzed, a further study on a higher number of samples will be required to see if the same results are arrived at. In addition, it is of utmost importance to carry out preliminary petrographic studies, which

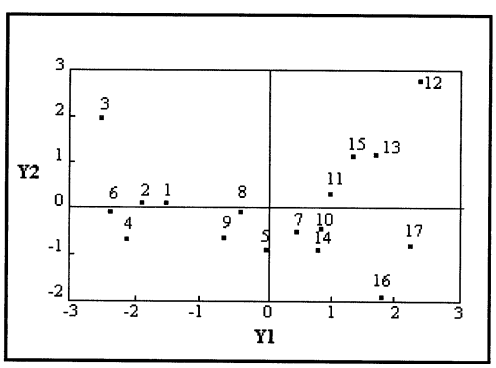

FIG. 4.
Centered coordinates in Y1–Y2.

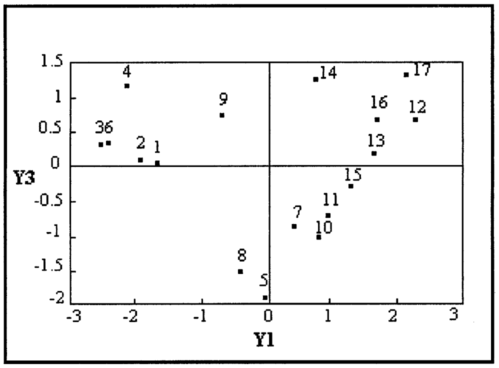

FIG. 5.
Centered coordinates in Y1–Y3.

would help in the initial diagnosis of the suitability of basaltic rocks to be used as aggregates in concrete, from the standpoint of their alkaline reactivity.

6. However, it should be borne in mind that in order to arrive at a final result on the alkali reactivity of aggregates, concrete and mortar accelerated test are required.

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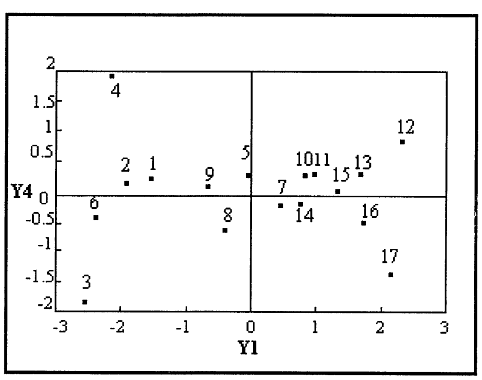

FIG. 6.
Centered coordinates in Y1–Y4.

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